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Effect of hole-induced shakedown in the Auger spectrum of lanthanum

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It is shown from the $M_{4,5}N_{4,5}X$ ($X = O_{1,2,3}, N_{6,7}$) Auger emissions of La metal, La_2O_3 , and LaF_3 that the $4f$ hole pulled down below the Fermi level by the $3d$ core hole in La metal is significantly populated before Auger decays take place. This extra relaxation mechanism by the $N_{4,5}VV$ Auger process from conduction electrons gives important contribution to the intensity of the $M_{4,5}N_{4,5}N_{6,7}$ Auger emission. The amount of this contribution can be calculated by existing theories on the shakeup or shakedown satellites on the La $3d$ core-level x-ray photoemission spectra (XPS) of these La compounds, and the results are found to be consistent with our experimental data. The criterion for the importance of this hole-induced shakedown process in the initial state of Auger spectra is determined, and the implications of this finding on other spectroscopies are discussed.

I. INTRODUCTION

Auger-electron spectroscopy (AES) has been traditionally used as a tool for element analysis, but recently attempts have been made to obtain chemical information as well. That is, Auger spectra involving valence levels (CVV or $CC'V$) are known to exhibit different line shapes depending on the bonding states of valence electrons, and these line shapes, if properly analyzed, can give information on the chemical bonding state of the atom. Considerable progress has been made lately in understanding these Auger line shapes involving valence electrons. Factors influencing Auger line shapes are usually classified into two categories¹—initial-state effect and final-state effect. The most important among these various factors are the screening effect in the initial core-hole state of the Auger process and the hole-hole Coulomb repulsion in the final state. The effect of the hole-hole interaction on the line shape of the Auger spectrum is now well understood.^{2,3} This final-state effect can distort the two-hole density of states or can give rise to a completely localized spectrum even though the valence electrons themselves are delocalized. The issue we are addressing here is the screening response of valence electrons in the initial state of Auger process where a core hole exists.

In the case of simple metals⁴ and transition-metal carbonyls,⁵ extensive theoretical calculations and experimental efforts have now established that the initial state of the Auger process is a fully screened state where the core hole is neutralized by extra screening valence electrons. This is reasonable in view of the fact that the final state of the main peak in the core-level x-ray photoemission spectroscopy (XPS), which becomes the initial state of Auger process in the x-ray excited Auger spectroscopy, corresponds to the fully screened states.⁶ However, for rare-earth elements with localized $4f$ electrons, there are two competing screening mechanisms^{7,8} for the deep core-hole created in the XPS. One is the screening by

delocalized ($5d, 6sp$) conduction electrons as in simple metals, and the other is the filling of the extra $4f$ level which was empty initially. Since the $4f$ level is more localized than $5d, 6sp$ orbitals, the latter screening mechanism usually gives a lower energy state than the former, and hence is called a “well screening” state as opposed to the “poorly screened” state of the former configuration. The principal energy gained by the $4f$ screening mechanism is the electrostatic Coulomb attraction energy between the core-hole and the $4f$ electron, and it is usually described as the “pulling-down” of the $4f$ level below the Fermi level E_F by the core hole.

Although this well screened state has the lowest energy in the presence of a core hole, it is an entirely different question whether this state is realized in the photoemission process when a core hole is created. The $4f$ level is quite localized and an electron in the conduction band has to be transferred to this localized $4f$ state to realize the well screened state. The probability for this process depends on the degree of hybridization between the $4f$ level and conduction-band states,^{9,10} and it is in fact the case that this probability is small for most rare-earth elements because the $4f$ wave function is quite localized. Hence the core-level XPS spectrum is usually dominated by the poorly screened peak, and the well screened peak shows up only as a small “shakedown satellite” in the lower binding-energy side¹¹ even in light rare-earth elements where the hybridization between $4f$ and conduction states is expected to be largest. The question then naturally arises whether the initial state of the Auger process in these systems is the poorly screened peak, which gives the “main peak” with strongest intensity in XPS spectrum, or the well screened peak which has the lowest energy. The question can be rephrased in terms of time scale as follows. Does the poorly screened state created in the photoionization process relax into the well screened state before Auger deexcitation process occurs? We shall show in this paper by comparing $M_{4,5}N_{4,5}N_{6,7}$

Auger spectra of La metal with those of La_2O_3 and LaF_3 that this relaxation indeed takes place and contributes significantly to the initial state of the Auger process in lanthanum metal.

II. EXPERIMENTAL PROCEDURES

The samples studied were La metal, La_2O_3 , and LaF_3 . X-ray photoemission spectra and x-ray excited Auger spectra were obtained with Mg $K\alpha$ or Al $K\alpha$ x-ray sources. The data on insulating La_2O_3 and LaF_3 compounds were taken with the Perkin-Elmer ESCA 560 system equipped with the cylindrical mirror analyzer at Seoul National University. These samples were commercially obtained powder (Johnson Matthey Inc., purity better than 99.99%) pressed into pellet form, and the pressure during the measurement was $\sim 1 \times 10^{-8}$ torr. No flood gun was used, and the data presented below are aligned so that carbon 1s line has a binding energy of 284.6 eV as a reference. The spectrum on La metal was taken with the AEI ES 200 spectrometer of the University of Groningen. The La metal sample was a thin film thermally evaporated *in situ* from an ingot. The base pressure during the measurement was $\sim 1 \times 10^{-10}$ torr, and no detectable oxygen contamination was found. All the spectra presented below were, unless stated otherwise, corrected for the x-ray satellites, the analyzer transmission, and the inelastic electron background by the usual method,¹² which assumes that the amount of inelastically scattered electrons is proportional to the number of primary electrons with higher kinetic energy.

III. DATA AND INTERPRETATION

Figure 1 shows La 3d core-level XPS spectra of LaF_3 and La_2O_3 . We see two pairs of peaks corresponding to the $3d_{3/2}$ (a, b) and $3d_{5/2}$ (a', b') core hole, where the peaks at lower binding energy (b, b') are traditionally called the "main peaks" and the higher binding energy peaks (a, a') are called the "shakeup satellites." The origin of the occurrence of these two peaks, main and shakeup satellite, is now well understood¹³ to arise from the pulling-down of the La 4f level in the presence of the 3d core hole, and the resulting hybridization between this 4f level and valence electronic states. Because of the rather strong hybridization in these insulating compounds, the assignment of one peak to the $|3d4f^0\rangle$ final state and the other to the $|3d4f^1 L\rangle$ shakeup state (here the underline denotes the hole and L means the ligand state) is not proper, and we should think of each peak as a superposition of both states with approximately equal weights.¹³ Hence the final states of La 3d core level XPS contain appreciable amount of 4f electrons (about $0.5e$ —see next section for details) induced by the core hole, and we expect to find Auger electrons emitted when the 3d core hole is filled by the 4f electron (e.g., $M_{4,5}N_{4,5}N_{6,7}$), although 4f electrons did not exist in the ground state of these compounds.

This expectation is indeed confirmed by the $M_{4,5}N_{4,5}X$ region of the Auger spectrum shown in Fig. 2. These spectra were taken with an Al $K\alpha$ source since the oxygen 1s peak overlaps in the region for spectra taken with

Mg $K\alpha$ source. We see there are four peaks labeled as a, b, c , and d in both LaF_3 and La_2O_3 , and the unknown level X can be deduced from the energy position of each peak. By assuming reasonable values of the electron correlation energy $U_{\text{eff}}(N_{4,5}, X)$ between the level X and 4d level ($U_{\text{eff}} \approx 7-10$ eV) we identified the level X by its energy position using the relation¹²

$$E_K(M_{4,5}N_{4,5}X) = E_B(M_{4,5}) - E_B(N_{4,5}) - E_B(X) - U_{\text{eff}}(N_{4,5}, X),$$

where E_K and E_B denote kinetic energy of the Auger electron and binding energy of the core hole, respectively. The assignment of each peak as determined above is as follows: peak a , $M_5N_{4,5}O_1$; peak b , $M_5N_{4,5}O_{2,3}$, $M_4N_{4,5}O_1$; peak c , $M_5N_{4,5}N_{6,7}$, $M_4N_{4,5}O_{2,3}$; peak d , $M_4N_{4,5}N_{6,7}$. This assignment of peaks is also consistent with the expected intensity ratio from the theoretical Auger transition-rate calculation¹⁴ (see next section for details). Here we neglected Auger processes involving delocalized valence levels largely made of oxygen 2p electrons, because being interatomic in nature and involving a delocalized level, this Auger peak is expected to be quite weak.¹⁴ What is remarkable in these spectra is the fact that we can see clearly identifiable peak d , which comes from the $M_4N_{4,5}N_{6,7}$ Auger transition. The 4f electron in this Auger process comes from the hybridization in the final state of 3d XPS as discussed above.

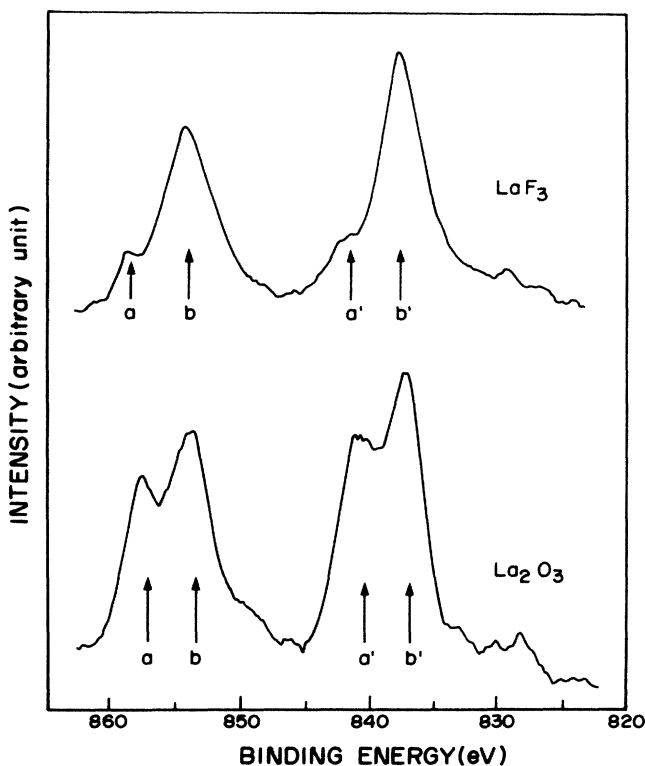


FIG. 1. La 3d core-level XPS spectra of LaF_3 and La_2O_3 . Both $3d_{3/2}$ (a, b) and $3d_{5/2}$ (a', b') are shown, and peaks a, a' are traditionally called the shakeup satellites and b, b' the main peak.

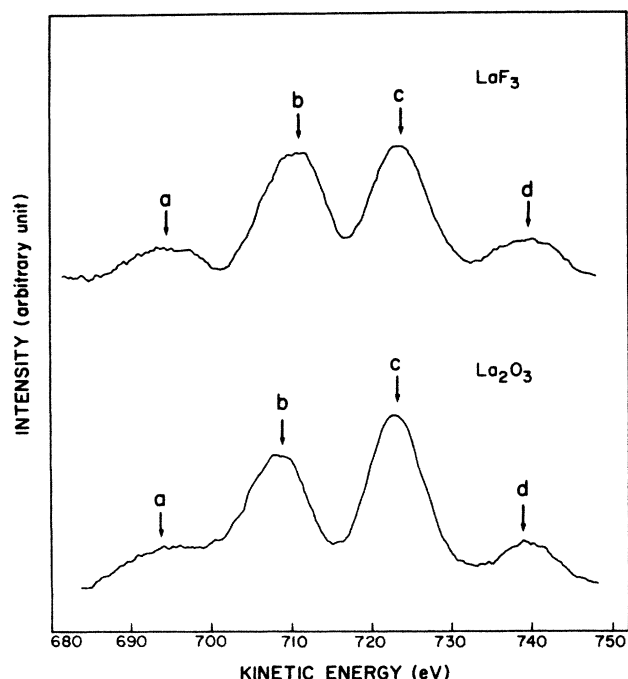


FIG. 2. X-ray-excited $M_{4,5}N_{4,5}X$ ($X=O_1, O_{2,3}$, and $N_{6,7}$ levels), Auger spectra of LaF_3 and La_2O_3 . The assignments of peaks are a , $M_5N_{4,5}O_1$; b , $M_5N_{4,5}O_{2,3}$ and $M_4N_{4,5}O_1$; c , $M_5N_{4,5}N_{6,7}$ and $M_4N_{4,5}O_{2,3}$; d , $M_4N_{4,5}N_{6,7}$.

In the case of La metal, the $3d$ core-level spectrum shows only a small intensity of shakedown peak containing $4f$ electron, as can be seen in Fig. 3. This spectrum is consistent with those reported earlier,^{11,13} and unlike the La_2O_3 or LaF_3 case the main peak a and the shakedown-satellite peak b correspond to the almost pure $|3d^9 4f^0\rangle$ and $|3d^9 4f^1 \underline{L}\rangle$ final state, respectively, since the hybridization between f and ligand levels is much smaller in metal than in insulators.¹³ The amount of $4f$ electron in this final state of La $3d$ XPS, judging from the intensity of the shakedown satellite is about $0.1e$ (see next section), much less than La_2O_3 and LaF_3 cases. Hence without an additional relaxation mechanism the $M_{4,5}N_{4,5}N_{6,7}$ Auger peak, in particular the one corresponding to peak d of Fig. 2, should become much smaller in La metal compared with La_2O_3 and LaF_3 . However, the Auger spectrum of Fig. 4 for La metal shows that this expectation is not realized, and peak d is almost as strong as in La_2O_3 or LaF_3 spectra, judging from its intensity compared to peaks a and b , which should be the same in all three compounds because they do not involve valence or $4f$ electrons. This is an indication that extra relaxation mechanism exists in the initial state of the Auger process for La metal, and that even though the shakedown satellite intensity is weak in the $3d$ XPS spectrum, it nevertheless contributes significantly to the Auger intensity. We will show in the next section that the intensity of peak d observed in Fig. 4 can be accounted for quantitatively by existing theories on $3d$ XPS satellites and the estimated $4f$ lifetime width of light rare-earth elements.

The fact that the $4f$ level which is pulled down by the

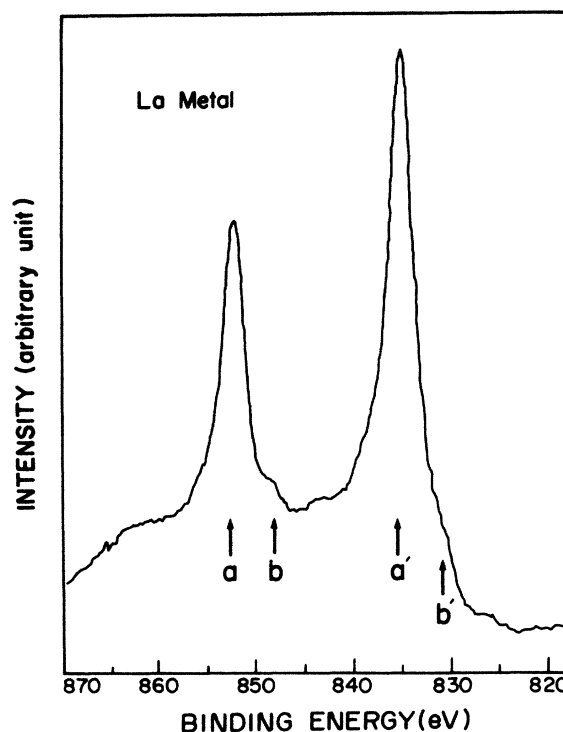


FIG. 3. La $3d$ core-level XPS spectra of La metal. Peaks a, a' are called the main peak and b, b' the shakedown satellite.

$3d$ core hole in La metal is significantly populated before the Auger decay takes place can also be seen by the $M_{4,5}N_{4,5}N_{4,5}$ Auger spectra. It is well known that Auger emissions starting from the deep core holes can be influenced by multiple-step decay processes.¹⁵ For instance, the intensity ratio of $L_2M_{4,5}M_{4,5}$ and

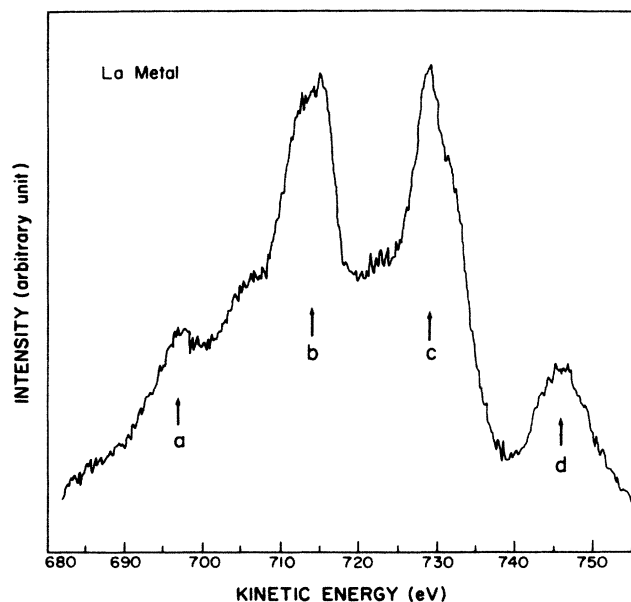


FIG. 4. X-ray-excited $M_{4,5}N_{4,5}X$ Auger spectra of La metal. The assignments of peaks are the same as in LaF_3 and La_2O_3 cases (see Fig. 2).

$L_3M_{4,5}M_{4,5}$ Auger peaks of Cu metal is not the expected statistical ratio of 1:2 due to the conversion of the L_2 hole into the L_3 hole by the $L_2L_3M_{4,5}$ Coster-Kronig process.¹⁶ The same kind of Coster-Kronig process $M_4M_5N_{6,7}$ can occur in La compounds between the M_4 hole and M_5 holes, and the degree of this conversion will also depend on the number of $4f$ electrons. But comparison of $M_{4,5}N_{4,5}N_{6,7}$ Auger spectra of La metal with those of LaF_3 and La_2O_3 (data not shown here) reveals that the degree of this conversion is quite similar in all three compounds. This fact again suggests that the number of $4f$ electrons in the initial state of the Auger process is not much different for all three La compounds, even though they have quite different $4f$ electron occupation numbers in the $3d$ XPS final states.

IV. QUANTITATIVE ANALYSIS

We will give the qualitative arguments of the preceding section a quantitative footing in this section with some simple calculations. First let us calculate the intensities of the $M_{4,5}N_{4,5}N_{6,7}$ Auger emissions expected when there is no extra relaxation mechanism between the creation of the $3d$ core hole in the photoionization process and the decay of this hole by the $M_{4,5}N_{4,5}N_{6,7}$ Auger process. Let us take the wave function of the ground state to be (in the cluster approximation)

$$|\psi_G\rangle = \alpha |4f^0\rangle + \beta |4f^1 \underline{}\rangle, \quad (1)$$

where $\underline{}$ denotes the hole in the valence band, and α, β are determined by the energy separation and hybridization between $4f$ and valence-band states. The two final states (main and shakeup) of the $3d$ core-level photoemission process can be taken as

$$\begin{aligned} |\psi_1\rangle &= \alpha' |3d^9 4f^0\rangle + \beta' |3d^9 4f^1 \underline{}\rangle, \\ |\psi_2\rangle &= \beta' |3d^9 4f^0\rangle - \alpha' |3d^9 4f^1 \underline{}\rangle. \end{aligned} \quad (2)$$

The intensities of the core lines in the sudden approximation are then

$$\begin{aligned} I_1 &\propto (\alpha\alpha' + \beta\beta')^2, \\ I_2 &\propto (\alpha\beta' - \beta\alpha')^2. \end{aligned} \quad (3)$$

From the energy separation and intensities of these two peaks, we can get the parameters of the following model Hamiltonian describing electron spectroscopic data:^{7,9,10,13}

$$\begin{aligned} H = & \sum_L \epsilon_L n_L + \epsilon_f \sum_m n_m + U_{ff} \sum_{\substack{m, m' \\ (m' > m)}} n_m n_{m'} \\ & + \epsilon_c n_c + (1 - n_c) U_{fc} \sum_m n_m + V \sum_{m, L} (a_m^\dagger a_L + a_L^\dagger a_m), \end{aligned} \quad (4)$$

where m and L denote quantum indices for the $4f$ and ligand states, respectively, U_{ff} and U_{fc} are Coulomb interactions between $4f$ - $4f$ or $4f$ -core levels, and V is the hybridization between the $4f$ and ligand state. Here we shall assume that hybridization is the same as in the ground state, but α', β' are different from α, β because the

energy separation changes in the final state due to the pulling-down of the $4f$ level by the $3d$ core hole. These parameters of the model Hamiltonian (4) have been determined for La metal, La_2O_3 , and LaF_3 in Ref. 13 from core-level XPS along with valence-band XPS and Bremsstrahlung isochromat spectroscopy (BIS) data. The model used there was the Anderson impurity Hamiltonian taking into account the band nature of ligand or conduction bands, but we shall adopt instead the simpler cluster model Hamiltonian [Eq. (4)] for our analysis here. We list in Table I the parameters of our Hamiltonian [Eq. (4)] consistent with the values determined in Ref. 13. Here ϵ_f ($4f$ level position), U_{ff} (correlation energy between $4f$ electrons), and U_{fc} (Coulomb attraction between core hole and $4f$ electron) values were taken from Ref. 13, while the $\sqrt{N_f} V(N_f)$ is the number of degeneracy, which is 14 in this case) value was determined to get the same ground-state $4f$ occupation number $\langle n_f \rangle_G$ as in Ref. 13. $\langle n_f \rangle_1 = \beta'^2$ and $\langle n_f \rangle_2 = \alpha'^2$ are $4f$ electron numbers in the $|\psi_1\rangle$ and $|\psi_2\rangle$ XPS final states, and I_1, I_2 are their intensities calculated from Eq. (3). If there is no extra relaxation of these XPS final states before Auger emission takes place, the $M_{4,5}N_{4,5}N_{6,7}$ Auger intensity would be proportional to the sum of $4f$ electron numbers in these two final states because both $|\psi_1\rangle$ and $|\psi_2\rangle$ can decay by this Auger process. This total number of $4f$ electrons, which is given by $\langle n_f \rangle_{\text{tot}} = I_1 \langle n_f \rangle_1 + I_2 \langle n_f \rangle_2$, is listed in the last column of Table I. We see that this total $4f$ electron number in the $3d$ XPS final states is about 5 times larger in LaF_3 and La_2O_3 than La metal. However, the comparison of the experimental Auger data in Figs. 2 and 4 shows that $M_{4,5}N_{4,5}N_{6,7}$ Auger emissions have similar intensities in La, LaF_3 , and La_2O_3 . This is an indication that extra relaxation mechanisms exist in the initial state of the Auger decay process.

What could be the extra relaxation mechanism? One obvious possibility is the $N_{6,7}VV$ Auger process involving conduction electrons, which fills the empty $4f$ level pulled down below E_F . In fact this process was found to be the dominant decay mechanism for the $4f$ holes of the rare-earth hexaborides¹⁷ created by photoionization. This decay probability becomes larger for light rare-earths because (1) the overlap of $4f$ electron with conduction electrons is larger since the $4f$ wave function is less localized and (2) the number of $4f$ holes is greater (larger degeneracy factor of the $4f$ level N_f). This $N_{6,7}VV$ decay process is not possible for LaF_3 because the $4f$ level in the presence of the $3d$ core hole is still above the valence band (see Table I), whereas it is certainly operative in La metal since the $4f$ level is pulled down 3.5 eV below E_F by the core hole. In the case of La_2O_3 , the $4f$ level in the XPS final state lies about 1 eV below the upper valence-band edge, but because of the shape of the insulator valence band and the shallowness of this $4f$ -level position, the contribution from this relaxation mechanism is expected to be small. Hence we will compare here the cases of LaF_3 and La metal.

To make an estimate on this extra relaxation contribution to the $M_{4,5}N_{4,5}N_{6,7}$ Auger emission intensity, we need to know the transition rate of the $N_{6,7}VV$ process by

TABLE I. The parameter values of the model Hamiltonian (4) for LaF_3 , La_2O_3 , and La metal determined from electron spectroscopic data. The meanings of symbols are as follows: ϵ_f , 4f-level energy position relative to the upper valence-band edge (LaF_3 and La_2O_3) or the Fermi level (La metal); U_{ff} , correlation energy between 4f electrons; U_{fc} , Coulomb attraction between the core-hole and 4f electron; N_f , the number of degeneracy for the 4f level; V , hybridization between the 4f level and delocalized valence electron levels; $\langle n_f \rangle_G$, 4f occupation number in the ground state; $\langle n_f \rangle_1, \langle n_f \rangle_2$, 4f electron number in the $|\psi_1\rangle$ and $|\psi_2\rangle$ 3d XPS final states; I_1, I_2 , intensities of $|\psi_1\rangle$ and $|\psi_2\rangle$ final states; and $\langle n_f \rangle_{\text{tot}} = I_1 \langle n_f \rangle_1 + I_2 \langle n_f \rangle_2$.

Compound	$\sqrt{N_f}V$ (eV)	ϵ_f (eV)	U_{ff} (eV)	U_{fc} (eV)	$\langle n_f \rangle_G$	$\langle n_f \rangle_1$	$\langle n_f \rangle_2$	I_1	I_2	$\langle n_f \rangle_{\text{tot}}$
LaF_3	2.5	14.5	8	-13.5	0.02	0.40	0.60	0.73	0.27	0.45
La_2O_3	2.5	10.7	8	-12	0.05	0.37	0.63	0.42	0.58	0.52
La	0.6	5.5	8	-9	0.01	0.03	0.97	0.92	0.08	0.10

which the 4f hole in the presence of the 3d core hole is filled by the conduction electrons. To measure this transition rate directly for La metal would be quite difficult, if not impossible, at present. However, we can estimate its magnitude from the lifetime width of the 4f hole of neighboring elements Ce or Pr. Here it is necessary to separate out the 4f level width due to the hybridization with conduction electrons, because the hybridization effect is already taken into account in the final states of 3d core-level XPS [Eqs. (1)–(3)]. For Ce compounds, the 4f-level width is probably dominated by the hybridization,¹⁸ but for Pr compounds the Auger lifetime widths of the 4f hole have been determined separately.^{18,19} They were found to be in the range 1.1–1.4 eV for PrAl_2 , $\text{Pr}_{0.9}\text{Th}_{0.1}$, and PrRu_2 . For La compounds the 4f hole width is expected to be larger due to the less localized 4f wave function and the larger degeneracy, but it will also vary from compound to compound. Considering all these uncertainties, we will take $\Gamma(N_{6,7}VV)$, the 4f hole lifetime due to the $N_{6,7}VV$ Auger process of La metal, as the difference between the experimental lifetime of the 3d_{5/2} XPS core line and the lifetime expected from the total calculated Auger transition rates¹⁴ originating from the M_5 hole. The difference is found to be small for Ba (~ 0.1 eV) but quite large for La (~ 1.2 eV), and was speculated to arise from the filling of the empty 4f level below E_F by $N_{6,7}VV$ Auger process.¹¹ Since the magnitude of this difference 1.2 eV [$\Gamma(\text{expt})=1.9$ eV $\Gamma(\text{theor})=0.7$ eV] is in the range expected from the Pr results, this supposition seems reasonable.

To compare experimental data of Figs. 2 and 4 with theoretical estimates, we also need transition rates of the individual Auger decay processes $M_{4,5}N_{4,5}X$ of M_4 and

M_5 holes. Unfortunately these rates have not been calculated to our knowledge for La, but results are available for the Nd atom.¹⁴ We list in Table II the theoretical lifetimes (\hbar times the inverse of the transition rates) of various Auger transitions of Nd relevant for our discussions here. To use these numbers for La we have to correct for the different number of 4f electrons (atomic Nd has four 4f electrons) and the difference in the total lifetime width of M_4, M_5 holes of Nd and La. These corrected numbers for La with one 4f electron are also listed in Table II. (Radiative transitions from $M_{4,5}$ holes in La are negligibly small¹⁴).

Now that we have relevant parameter values, we can get quantitative estimates of the $M_{4,5}N_{4,5}N_{6,7}$ Auger emission intensities for LaF_3 and La metal as follows. First, let us consider LaF_3 , where there is no extra relaxation mechanism in the initial state of the Auger process. The percentage $R(M_4N_{4,5}N_{6,7})$ of the M_4 hole decay by the $M_4N_{4,5}N_{6,7}$ Auger process is given by

$$R(M_4N_{4,5}N_{6,7}) = R_1(\text{from } |\psi_1\rangle \text{ XPS final state}) + R_2(\text{from } |\psi_2\rangle \text{ XPS final state}), \quad (5)$$

where

$$R_1 = I_1 \left[\beta'^2 \frac{\Gamma(M_4N_{4,5}N_{6,7})}{\Gamma(M_4)} \right] \quad (6a)$$

and

$$R_2 = I_2 \left[\alpha'^2 \frac{\Gamma(M_4N_{4,5}N_{6,7})}{\Gamma(M_4)} \right] \quad (6b)$$

TABLE II. Theoretical transition rates of various Auger processes from the M_4 or M_5 hole of a Nd atom (from Ref. 14), and corresponding values for a La atom with one 4f electron. The values for La were obtained from Nd values by (i) dividing by 4 if the Auger process involves 4f level and (ii) multiplying by the ratio of total theoretical lifetime width between La and Nd for the M_4 or M_5 hole.

Auger process (M_4 shell)	Theoretical lifetime (eV)		Auger process (M_5 shell)	Theoretical lifetime (eV)	
	Nd	La		Nd	La
$M_4N_{4,5}O_1$	0.012	0.010	$M_5N_{4,5}O_1$	0.012	0.010
$M_4N_{4,5}O_{2,3}$	0.032	0.027	$M_5N_{4,5}O_{2,3}$	0.032	0.027
$M_4N_{4,5}N_{6,7}$	0.098	0.020	$M_4N_{4,5}N_{6,7}$	0.098	0.020
$M_4N_{4,5}N_{4,5}$	0.40	0.33	$M_5N_{4,5}N_{4,5}$	0.40	0.33
$M_4M_5N_{6,7}$	0.37	0.077			

Here $\Gamma(M_4)$ and $\Gamma(M_4N_{4,5}N_{6,7})$ denote the total lifetime of the M_4 hole and the lifetime due to the $M_4N_{4,5}N_{6,7}$ Auger process, respectively, and $I_1 = (\alpha\alpha' + \beta\beta')^2$, $I_2 = (\alpha\beta' - \beta\alpha')^2$ are intensities of $|\psi_1\rangle$ and $|\psi_2\rangle$ XPS final states. We can rewrite this expression as

$$R = \langle n_f \rangle_{\text{tot}} \frac{\Gamma(M_4N_{4,5}N_{6,7})}{\Gamma(M_4)},$$

where $\langle n_f \rangle_{\text{tot}}$ is the total number of 4f electrons in the XPS final state, which is listed in the last column of Table I. The percentage of decay to other Auger processes not involving a 4f electron, $R(M_4N_{4,5}O_1)$ for example, is simply given by

$$\begin{aligned} R(M_4N_{4,5}O_1) &= I_1 \frac{\Gamma(M_4N_{4,5}O_1)}{\Gamma(M_4)} + I_2 \frac{\Gamma(M_4N_{4,5}O_1)}{\Gamma(M_4)} \\ &= \frac{\Gamma(M_4N_{4,5}O_1)}{\Gamma(M_4)}. \end{aligned} \quad (7)$$

The Auger intensities originating from the M_5 hole are also given by similar expressions, but should be multiplied by 1.5 to account for the degeneracy ratio between M_4 and M_5 holes.

For La metal there is the extra contribution from relaxation processes, and the decay probability of the M_4 hole by the $M_4N_{4,5}N_{6,7}$ Auger process is the sum of two contributions:

$$R(M_4N_{4,5}N_{6,7}) = R^{\text{dir}}(M_4N_{4,5}N_{6,7}) + R^{\text{relax}}(M_4N_{4,5}N_{6,7}), \quad (8)$$

$$R(M_4N_{4,5}O_1) = R^{\text{dir}}(M_4N_{4,5}O_1) + R^{\text{relax}}(M_4N_{4,5}O_1)$$

$$\begin{aligned} &= \frac{\Gamma(M_4N_{4,5}O_1)}{\Gamma(M_4)} + I_1 \left[\alpha'^2 \frac{\Gamma(N_{6,7}VV)}{\Gamma(M_4)} \right] \left[\frac{\Gamma(M_4N_{4,5}O_1)}{\Gamma(M_4) - \Gamma(N_{6,7}VV)} \right] \\ &+ I_2 \left[\beta'^2 \frac{\Gamma(N_{6,7}VV)}{\Gamma(M_4)} \right] \left[\frac{\Gamma(M_4N_{4,5}O_1)}{\Gamma(M_4) - \Gamma(N_{6,7}VV)} \right]. \end{aligned} \quad (10)$$

Using the values of $\Gamma(M_4N_{4,5}X)$, $\Gamma(M_5N_{4,5}X)$ listed in Table II corrected for La and $\Gamma(N_{6,7}VV) = 1.2$ eV, we can now calculate decay probabilities for all states X shown in the experimental Auger spectra of Figs. 2 and 4. There is one more correction we have to make before comparing with experimental data—the Coster-Kronig conversion of the M_4 hole into the M_5 hole¹⁶ by the $M_4M_5N_{6,7}$ Auger process discussed earlier. This probability can be calculated by equations similar to Eqs. (8) and (9) by simply substituting $\Gamma(M_4N_{4,5}N_{6,7})$ by $\Gamma(M_4M_5N_{6,7})$, and we find that about 4% (LaF₃ case)–5% (La metal case) of the M_4 hole is converted to the M_5 hole. We list in Table III the results of our calculations for decay probabilities to various Auger final states in LaF₃ and La metal including Coster-Kronig conversion corrections. Strictly speaking, $M_4M_5N_{6,7}$ Auger-preceded $M_5N_{4,5}X$ final states are different from

where $R^{\text{dir}}(M_4N_{4,5}N_{6,7})$ is the direct probability utilizing 4f electrons in the final state of the 3d XPS and $R^{\text{relax}}(M_4N_{4,5}N_{6,7})$ is the contribution after the 4f level is filled by the extra relaxation process $N_{6,7}VV$. $R^{\text{dir}}(M_4N_{4,5}N_{6,7})$ can be calculated by an expression similar to Eq. (6), whereas to calculate $R^{\text{relax}}(M_4N_{4,5}N_{6,7})$ we consider the following two-step process:

M_4 hole \longrightarrow filling of the empty 4f hole by $N_{6,7}VV$ process \longrightarrow decay by $M_4N_{4,5}N_{6,7}$ Auger process.

The probability for this process is given by

$$\begin{aligned} R^{\text{relax}}(M_4N_{4,5}N_{6,7}) &= I_1 \left[\alpha'^2 \frac{\Gamma(N_{6,7}VV)}{\Gamma(M_4)} \right] \left[\frac{\Gamma(M_4N_{4,5}N_{6,7})}{\Gamma(M_4) - \Gamma(N_{6,7}VV)} \right] \\ &+ I_2 \left[\beta'^2 \frac{\Gamma(N_{6,7}VV)}{\Gamma(M_4)} \right] \left[\frac{\Gamma(M_4N_{4,5}N_{6,7})}{\Gamma(M_4) - \Gamma(N_{6,7}VV)} \right]. \end{aligned} \quad (9)$$

The reason for subtracting $\Gamma(N_{6,7}VV)$ in the last denominators is because $N_{6,7}VV$ decay is not possible once the 4f hole is filled. (Double occupation of 4f hole would be energetically forbidden.) The decay probabilities to other Auger processes not involving a 4f electron can be calculated similarly, hence $R(M_4N_{4,5}O_1)$ for example is given by

ordinary $M_5N_{4,5}X$ Auger final states. However, the difference in energy is small and in our broad experimental Auger data we cannot clearly distinguish between them. Therefore we added them in the experimental intensities listed to the right of the theoretical values of Table III. These numbers in the “Expt.” column are not absolute decay probabilities of the M_4 or M_5 holes because we cannot accurately calibrate the number of M_4 or M_5 holes. Instead these numbers were calculated from relative intensities of peaks a , b , c , and d in the spectra and requiring that the total probability should be equal to the theoretical total probability in the left column. Therefore only the relative intensities are meaningful.

We note from Table III that the agreement between theory and experiment is reasonable, especially considering the uncertainty of the $\Gamma(N_{6,7}VV)$ value. In particular, the experimental intensity ratios among peaks a , b , c ,

TABLE III. Decay probabilities to $M_{4,5}N_{4,5}X$ ($X = O_1$, $O_{2,3}$, and $N_{6,7}$ level) Auger processes for LaF_3 and La metal. Theoretical values were determined as described in the text, and experimental values were obtained from spectra shown in Figs. 2 and 4.

Auger process	Material		LaF ₃		La metal	
	Theory		Expt.		Theory	
$M_5N_{4,5}O_1$	0.020 (Peak <i>a</i>)	0.020	0.017		0.020	0.020
$M_4N_{4,5}O_1$	0.012	(Peak <i>b</i>)	0.067	0.063	0.013	0.068
$M_5N_{4,5}O_{2,3}$	0.055				0.055	
$M_4N_{4,5}O_{2,3}$	0.034	(Peak <i>c</i>)	0.052	0.059	0.034	0.060
$M_5N_{4,5}N_{6,7}$	0.018				0.026	
$M_4N_{4,5}N_{6,7}$	0.011 (Peak <i>d</i>)	0.011	0.013		0.016	0.016

and *d* are as expected from theoretical calculations, justifying our assignment of these peaks by energy positions alone. Secondly, theory now predicts that the $M_4N_{4,5}N_{6,7}$ Auger emissions (peak *d*) have similar intensities for LaF_3 and La metal, in agreement with experimental data. Without an extra relaxation contribution from $N_{6,7}VV$ Auger process in the initial state of Auger decay, theory would predict that this peak in La metal has only 20% of the intensity compared with that in LaF_3 . This analysis proves the importance of extra relaxation contribution in the Auger decay process.

V. SUMMARY AND DISCUSSIONS

We have shown by studying $M_{4,5}N_{4,5}X$ ($X = O_1, O_{2,3}, N_{6,7}$) Auger intensities of La metal, LaF_3 , and La_2O_3 that if the $3d$ core hole pulls down the $4f$ hole below the conduction band as in La metal, this empty $4f$ level is significantly populated to give a well screened initial state before the Auger decay processes take place. This can be understood quantitatively from existing theories on the $3d$ core-level XPS shakeup and shake-down peaks, and we have estimated the lifetime of this extra relaxation $N_{6,7}VV$ Auger process in La metal to be ~ 1.2 eV. Qualitatively, the extra relaxation contribution becomes important when the lifetime of the $3d$ core hole is not too short compared with the lifetime of the empty $4f$ hole. Since, as we go to heavier rare earths the $3d$ hole lifetime rapidly decreases, whereas $\Gamma(N_{6,7}VV)$ becomes small due to the more localized $4f$ wave function

and the reduced number of $4f$ holes, this extra relaxation contribution will become less important. It will be interesting to determine at which element this contribution becomes insignificant.

Our finding here is consistent with the earlier report on the hole-induced shakedown effect in the $M_{4,5}$ fluorescence emission spectrum of La metal.²⁰ This is also a direct consequence of the lifetime due to the $N_{6,7}VV$ Auger process being comparable to $\Gamma(M_4)$ or $\Gamma(M_5)$. A similar extra relaxation mechanism has been found to be operative in the decay of the core hole of adsorbed molecules. Chen *et al.*²¹ found by studying the kinetic energy distribution of the electrons emitted by the radiationless decay of the carbon $1s$ hole of CO adsorbed on Cu(110) that all excited core-hole configurations created by the initial photoionization process decay to the fully screened core-hole state before the core hole decays. This relaxation effect should be taken into account when interpreting some spectroscopic data, for example, when using appearance potential spectroscopy (APS).²²

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